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(71) Applicant
Colgate-Palmolive Company (USA-Delaware),
300 Park Avenue, New York, New York 10022, United
States of America

(72) Inventors
Edward A. Tavss,
John Santalucia,
Victor Temnikow

(74) Agent and/or Address for Service
Kilburn & Strobe, 30 John Street, London WC1N 2DD

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(54) Substrate containing
polypropylene and articles made
therefrom

(57) There is disclosed a substrate of
layers (11, 16) of polypropylene having
sandwiched therebetween a metal foil
layer (13) and a paper layer (15) all
suitably adhered to one another. The
substrate may be employed in
fabricating a dentifrice tube.

FIG. 1

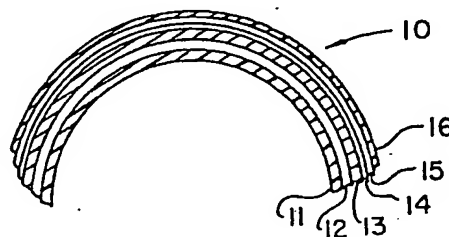


FIG. 1

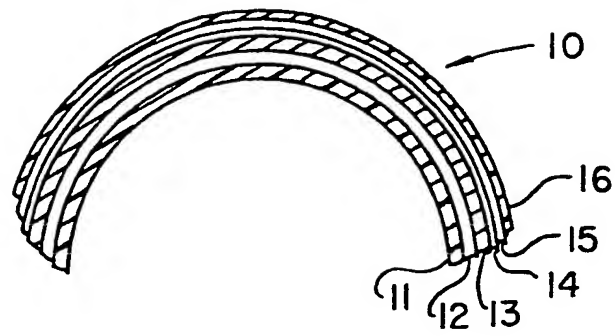
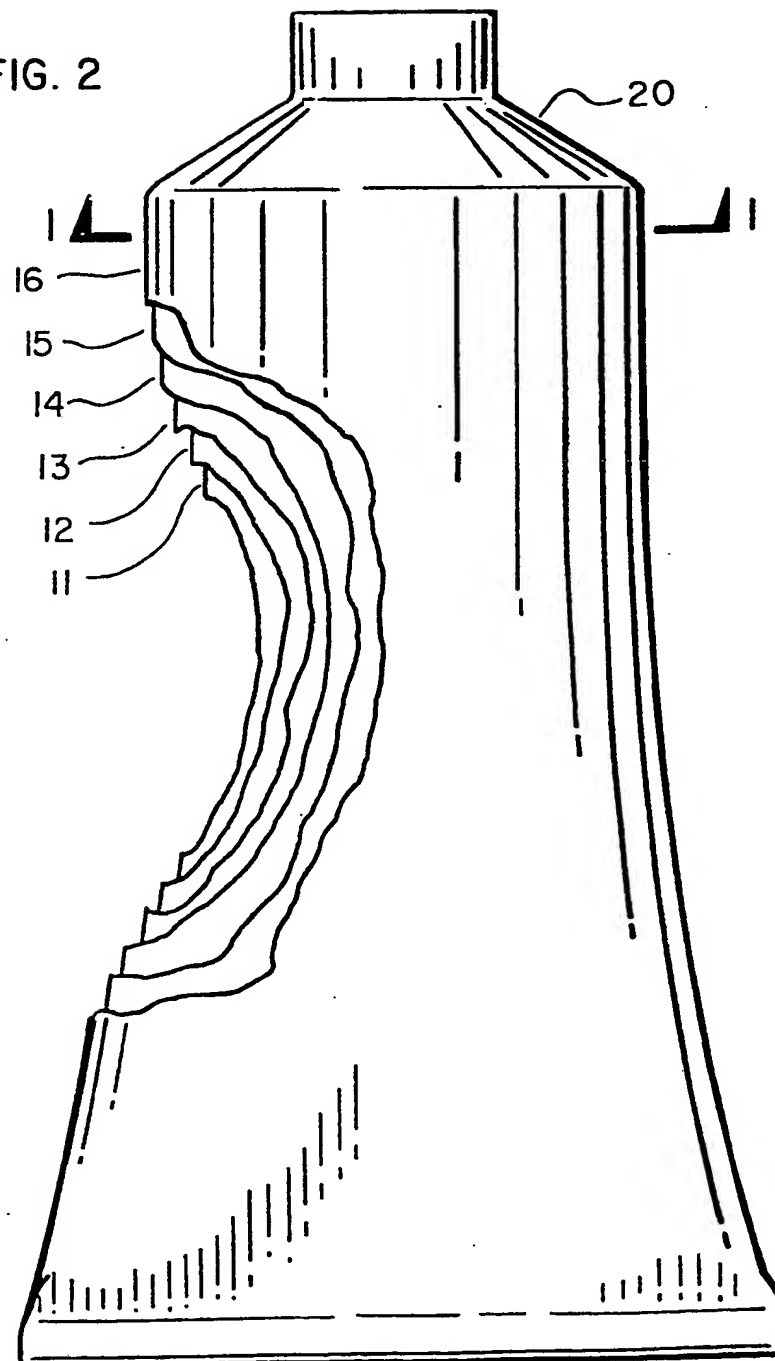


FIG. 2



SPECIFICATION

Substrate containing polypropylene and articles made therefrom

- 5 The present invention relates broadly to the container art, and is more particularly concerned with a col- 5
lapsible dispensing container of laminated wall construction in the body portion thereof, whereby prod-
uct permeation and absorption, and oxygen absorption are substantially prevented in all regions of the
container structure susceptible thereto.

Collapsible tubes formed of metallic and plastic materials have long been known in the packaging field.

- 10 Extruded metal tubes are inherently brittle and repeated use not infrequently results in wall cracks so 10
that the product is exuded from a location other than the essentially rigid dispensing orifice. Of the prior
art metal tubes, aluminium tubes, while probably being the least brittle, are somewhat limited in their
applications since up to the present time it has not been possible to apply to the interior surfaces thereof
a completely satisfactory coating, when required to prevent attack and corrosion of the metal by alkaline
15 or acid contents and contamination of the contents by the reaction products. Notwithstanding the rela- 15
tively brittle nature of a metal tube, the mentioned internal coating operation requires an additional proc-
essing step which necessarily increases the cost of the final article.

- Tubes formed of polyethylene and other plastic materials have enjoyed wide commercial success in
the packaging of many products; however, certain other products after a time have been noted to deteri-
20 orate when contained therein. Plastics as exemplified by polyethylene are permeable to a degree when 20
employed in the wall thicknesses used in tubular containers, and the essential oils embodied in most
dentifrices for flavouring purposes are reduced in volume during storage of the container, rendering the
dentifrice less palatable. Also, the plastic container wall absorbs oxygen over a period of time and ulti-
mately may decompose the product, which has actually been found to be the case with fluoride-contain-
25 ing toothpastes. A further disadvantage of a plastic tube resides in the inability of the surface to readily 25
receive printing or decorative material. In addition, plastic tubes, as exemplified by polyethylene, have a
memory effect; that is, they do not remain compressed when squeezed, a particular disadvantage for
dentifrice tubes.

- To counter the above problems, it has accordingly been proposed to provide a metallic foil barrier be-
30 tween the product and the polyethylene tube body. This would counter the compressibility problem in 30
that the metal layer would impose its compressibility upon the plastic. In addition, the metallic foil barrier
between the product and the polyethylene tube body would prevent the mentioned loss of essential oils
and the absorption of oxygen. The metallic barrier has been suggested as an interlayer between facing
sheets of polyethylene, and that a laminate be formed by heat or without suitable adhesives. However,
35 while a structure of this general character is effective to prevent some product permeation and oxygen 35
absorption through the tube body, and particularly when the inner thermoplastic layer is a copolymer of
ethylene olefin and a polar group containing monomer which is co-polymerisable therewith, there re-
mains the possibility of product deterioration albeit to a much lesser extent.

Attention is directed to the following prior art:

- 40 Marchak (Canadian Patent No. 728,525) discloses a laminated tube containing an inner layer of polyeth- 40
ylene. He recognised the problem of absorption of flavour oil by the thermoplastic wall, and suggested
the use of nylon to overcome this.

- Herrero (U.S. Patent No. 4,139,665) discloses a laminate which does not contain metal. This laminate
used polypropylene, among others, as the inner layer, in order to act as a barrier against moisture and
45 water vapour. A thermoplastic acrylonitrile copolymer serves as the flavour barrier. This laminate is dif- 45
ferent from the present invention in that it does not contain a metallic foil. Furthermore, Herrero failed to
recognise the efficacy of polypropylene as a flavour barrier.

- Yoshio et al (U.S. Patent No. 3,958,721) teach a collapsible, laminated tube which also does not contain
a metal sheet. Although this tube contains polypropylene, they note that the low permeability to odour
50 and the high resistance to oil is provided by the polyvinyl alcohol film. 50

None of the above cited references specifies polypropylene as the inner layer of collapsible laminated
tubes containing metallic foils. In those cases in which polyolefins are mentioned, no indication is made
of high resistance to absorption of essential flavour oils. In fact, the problem with polyethylene is its high
flavour absorption.

- 55 It has been demonstrated herein, surprisingly, that polypropylene, a chemical closely related to poly- 55
ethylene, has substantially reduced absorption of flavour oils. The tube contains polypropylene as the
innermost and outermost layers, paper, aluminium foil, and adhesive, as intermediate layers.

The present invention aims to provide a collapsible dispensing container of laminated wall construction
in the body portion.

- 60 The present invention also aims to provide a tubular container having a plurality of adherent layers in 60
the body portion thereof, one of said layers providing a barrier to product migration and oxygen absorp-
tion such as metallic foil and another of said layers being polypropylene or a copolymer or mixture
thereof varying in density and crystallinity or both. The polypropylene layer being innermost and prefera-
bly another such layer also being disposed as the outside layer with different additional laminae sand-
65

Such additional layers may comprise paper and suitable adhesive and bonding agents such as copolymer of ethylene and acrylic acid. The collapsible dispensing container of the present invention may be constructed from the laminated substrate of the present invention by conventional and known apparatuses. Examples of suitable equipment and a suitable method are claimed in U.S. Patent No. 3,832,964, which is incorporated herein by reference.

The procedure described in U. S. Patent No. 3,832,964 involves wrapping a sheet of flexible material (in the present case this will be the material of the present invention) about a mandrel and fastening overlapping side edges together to provide a tubular body having a longitudinal seam (which can be done readily with the material of the present invention because the materials of the inner and outer faces being the same can readily be bonded to each other) and then inserting and clamping one end of the formed body shell between an outer head structure element e.g. affording a neck and shoulders with an outer thread on the neck and an inner head structure element, e.g. affording an inner neck and shoulders.

These components may conveniently be formed of or coated on their sheet contacting faces with the polymer of the outer layer of the laminate of the present invention.

A further object of the present invention is to provide a method of producing laminated tubes in which a tubular body is formed of a barrier layer and a polypropylene or copolymer thereof laminated thereto; the laminated tube body is then located on a forming member juxtaposed to a barrier member also positioned thereon.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples and drawings, in which:-

Figure 1 is a cross-sectional view of a fragmentary portion of a laminated substrate of the present invention; and

Figure 2 is a side elevational view of a collapsible dispensing container embodying the novel concepts of the present invention, with portions of the body walls being broken away to more fully illustrate the laminated structure.

In the drawings like numerals are employed to designate like parts throughout the drawings.

Referring now first to *Figure 1* of the drawings, a substrate 10 is shown in cross-section to reveal the components of the sandwich that go to make up the laminated configuration.

The bottommost layer 11 is a polypropylene. The second layer 12 thereabove is an adhesive layer which joins the polypropylene layer 11 to a third layer 13 which is a metal foil such as aluminium foil. The fourth layer 14 is another adhesive that adhesively secures the other surface of the metal foil layer 13 to a paper layer 15. The topmost layer 16 is polypropylene.

The polypropylene is particularly useful because it has very low flavour absorption characteristics as can be seen from the following tables where polypropylene is compared with polyethylene where the thicknesses of the layers of coating are the same.

Example 1

Samples of polymer were tested by a total immersion procedure (gravimetric-irregular pieces). A sample piece of the polymer to be tested is weighed and placed in a glass jar. Sufficient neat flavour oil to totally immerse the sample is introduced into the jar. The sample is aged for two weeks at 72°F (°C). The sample is removed, dried and weighed to determine the uptake of flavour oil. The increase in weight (absorption) is given as a percentage of the original weight of the sample in Table 1 below.

TABLE 1

Polymer Absorption of Neat Flavour Oil

		Absorption (%)	
50	Polypropylene Tenite 4230G (Eastman)	1.3	50
	Polypropylene F120F (United States Steel)	1.6	
55	Polypropylene FP200F (United States Steel)	2.3	55
	Polypropylene Vestrolen P3200 (Huls Plastic)	2.3	
60	Low density polyethylene Tenite 154 (Eastman)	5.5	60
65	Low density polyethylene Lupolen 1804H (BASF)	5.6±0.14	65

Example 2

Various polymers were tested. Table 2 below gives the amount of flavour oil lost by the dentifrice relative to that lost by the Bayer low density polyethylene, the value for which was arbitrarily set at 100.

It will be appreciated that the lower the number the less flavour is lost from the dentifrice.

TABLE 2

Loss of Flavour From Flavoured Dentifrice into Polymers

		Flavour Loss	
10	Polypropylene Tenite 4230G(Eastman)	31	10
	Polypropylene F120F (United States Steel)	38	
15	Polypropylene F200F (United States Steel)	38	15
	Low density polyethylene Lupolen 1804H (BASF)	100	
20	Low density polyethylene Tenite 154 (Eastman)	130	20

Example 3

Various polymers were tested at various temperatures given in Table 3 below for 3 months and the flavour absorbed by each polymer after that time and at that temperature relative to that absorbed by the Bayer low density polyethylene at 72°F (°C) is given in Table 3. The value of the Bayer low density polyethylene was arbitrarily set at 100.

It will be appreciated that the lower the number the less is the flavour absorbed.

TABLE 3

Relative Flavour Absorption into Polymers From Flavoured Dentifrice

		72°F (°C)	90°F (°C)	120°F (°C)	
35	Aluminium	0	0	0	35
40	Polypropylene FP200F (United States Steel)	34	51	55	40
	Polypropylene F120 (United States Steel)	55	68	73	
45	Low density polyethylene NPE853 (Norchem)	69	76	104	45
50	Low density polyethylene Lupolen 1804H (BASF)	100±19	107±14	119±10	50

The adhesives may be a copolymer of ethylene and acrylic acid or methacrylic acid, or sodium or zinc salts thereof in a diluent system.

The metal foil is preferably aluminium foil.

The paper layer is desirably a kraft paper.

The thickness range of each of the layers is as follows:

Polypropylene layer 11 - 0.5 mils to 3.0 mils (. . . mm to . . . mm), preferably 1.0 mils (. . . mm).

Adhesive layer 12 - sufficient to assure adherence.

Metal foil layer 13 - 0.5 mils to 2.0 mils (. . . mm to . . . mm), preferably 1.0 mils (. . . mm).

Adhesive layer 14 - sufficient to assure adherence.

Paper layer 15 - 1.5 mils to 2.5 mils (. . . mm to . . . mm), preferably 2.0 mils (. . . mm).

Polypropylene layer 16 - 3.5 mils to 5.0 mils (. . . mm to . . . mm), preferably 4.0 mils (. . . mm).

The topmost polypropylene layer 16 is adhered to the paper layer 15 by means of the application of sufficient heat and pressure to the substrate. In the event the application of heat and pressure is not

appropriate a suitable adhesive is employed. Figure 2 is an example of the laminated structure of a roll

lapsible container with the layers being demonstrated as in Figure 1 with layer 11 being innermost and the other layers being of the same materials and in the same order as shown.

It is believed manifest from the foregoing that applicant has provided a collapsible container structure which substantially reduces the problems heretofore unsolved by the prior art. The laminated substrate and a barrier shoulder piece 20 substantially eliminates product permeation and oxygen absorption.

The outer layer of polypropylene is a thermoplastic capable of fusion during a side seaming step and granting adequate protection to the paper and metallic foil interlayer. The art of seaming of a collapsible dentifrice tube of the general type herein disclosed can be seen in U.S. Patent No. 3,295,725, incorporated herein by reference. However, the outer layer of polypropylene and paper may be eliminated if the foil barrier is of sufficient thickness to resist damage, and by flowing a thermoplastic material into the overlap side seam during the sealing thereof when such a system is employed.

Further, the outer layer may be paper in a three-ply laminate formed of paper, foil and a polypropylene and copolymer thereof as described. As the outermost and innermost layers are preferably the same, the folded edges of the tube produced from the substrate is conveniently heat bonded. A suitable adhesive can be used when heat bonding is not possible. This modification is in addition to the aforementioned four-ply laminate comprised of from outside to in, polypropylene, paper, foil and polypropylene. It is contemplated that suitable adhesives will be employed between the laminae whenever necessary.

Polypropylene can also be employed for the shoulder piece, cap, neck, piston and in the construction of dispensing valves for other dentifrice dispensers, particularly in conjunction with the interior portions, exposed to the contained dentifrice, and, again, where required, compatible adhesives would naturally be employed.

Additionally when cast as a film on the interior surfaces of fibre drums used for the storage of flavoured dentifrices, the material will retard flavour loss into the drums, hereby extending storage life.

Various modifications of the invention have been disclosed herein, and these and other changes can, of course, be effected without departing from the novel concepts of the present invention.

CLAIMS

1. A substrate of layers of materials comprising a first layer of a polypropylene, a second layer of metal foil, a third layer of paper and a fourth layer of a polypropylene.

2. A substrate as claimed in Claim 1 in which the first layer of the polypropylene is secured to the metal foil with an adhesive.

3. A substrate as claimed in Claim 1 or Claim 2 in which the third layer of paper is secured to the fourth layer of the polypropylene with an adhesive.

4. A substrate as claimed in Claim 2 or Claim 3 in which the adhesive is a copolymer or ethylene and acrylic acid.

5. A collapsible paste dispensing container of layers of materials comprising a first innermost layer of polypropylene, a second layer of metal foil, a third layer of paper and an outermost fourth layer of polypropylene.

6. A container as claimed in Claim 5 in which the first layer of the polypropylene is secured to the metal foil with an adhesive.

7. A container as claimed in Claim 5 or Claim 6 in which the third layer of paper is secured to the fourth layer of the polypropylene with an adhesive.

8. A container as claimed in Claim 6 or Claim 7 in which the adhesive is a copolymer of ethylene and acrylic acid.

9. A container as claimed in any one of Claims 1 to 8 containing a composition containing one or more flavour oils.

10. A container as claimed in Claim 9 in which the composition is a dentifrice composition.

11. A package containing a composition containing one or more flavour oils, the interior surfaces of the package in contact with the said composition being afforded by polypropylene.